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(54) Producing coloured images in plastics materials

(57) A process for producing coloured images in plastics objects of any desired shape, which process comprises
a) coating the object to be marked with a soluble lacquer film containing at least one colouring component,
b) irradiating the coated object, after drying said film, with a continuously excited laser such that the film and the surface of the object directly adjacent soften at the irradiated areas and the colouring component penetrates the surface of the plastics object, and
c) dissolving the residual non-irradiated film with a solvent such that a visual coloured image remains at the irradiated areas of the plastics object.

Preferably the plastics for the object is an acrylic polymer, polyester or a polycarbonate; the laser is preferably a CO_2 laser or an argon laser.

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Coloured laser marking of plastics materials

The present invention relates to a process for the coloured laser marking of plastics objects of any shape and to the object so marked.

It is known to mark plastic objects by irradiation with a laser beam to produce a colour contrast marking at the irradiated areas. Thus, for example, in European patent application 0 036 680 the proposal is made to mark an object, at least one part of the surface of which consists of a synthetic resin material, with a laser beam of a specific intensity. The material to be marked contains a dye and a silicon-containing inorganic compound or a dye comprising silicon, which dye is decomposed by irradiation with the laser beam, thereby resulting at the irradiated areas in the formation of a white mark which is in good contrast with the non- irradiated coloured part of the material.

It is also known to mark plastics parts with a colour contrast marking. For example, European patent application 0 190 997 teaches a method of marking organic materials of high molecular weight in the form of parts, sheets or films, which method comprises the use of an additive that effects a change in colour by irradiation with a laser beam, for example an inorganic or organic pigment, such that a change in colour, normally black, white or beige, occurs at the irradiated site of the material.

Japanese Patent Kokai Sho 60-155 493 also relates to the laser beam marking of plastics parts or films. The method employed comprises producing a colour contrast marking by incorporating in the plastics material a yellow iron oxide, which material may or may not contain a further yellow, yellowish-green or red pigment. When the plastics material is irradiated by a laser beam, the yellow iron oxide turns red at the irradiated areas such that red, orange or brown marks are produced.

Further, Japanese patent application 58-210 937 discloses synthetic resin compositions for laser marking, which compositions contain two different colorants, one of which volatilises, discolours or changes colour on irradiation with a laser beam, and the other remains unchanged, such that a coloured mark is formed. A number or organic pigments

and dyes are cited as examples of colorants that undergo colour change, whereas a number of inorganic pigment are cited as stable compounds. This publication is silent as regards types of laser, energy, intensity, wavelength and pulse duration.

Finally, GB patent specification 1 353 063 proposes a process for the laser marking of objects made of metal, plastics, paper, wood, glass ceramics or concrete, which comprises irradiating with a laser beam an unbound layer of light-absorbing particles applied to the surface of the object to be marked. Irradiation effects retention of the layer of unbound particles in the object at the irradiated, fused areas, and the remaining non-irradiated and non-retained particles are then removed in conventional manner. According to this publication, inorganic or organic pigments, mixtures of pigments with a resin, coloured high molecular weight material or metal powders may be used as particles. A drawback of this process is that, during marking, the layer of unbound particles applied to the article is often blown away from the surface of said object at the irradiated areas, so that no distinct marking can be produced. Moreover, applying the particles in the form of a uniform, thin layer, especially to non-level surfaces, is not easy to accomplish in actual practice. In addition, the coated objects must be treated with extreme caution prior to marking in order that the particle layer may not be damaged.

The methods and synthetic resin compositions referred to above do not, however, meet the present requirements of practice in all respects. Usually the surface of the marked material is damaged at the irradiated areas, resulting in unwanted grooves, indentations or scratches and, in addition, in marks of insufficient general qualities such as insufficient abrasion- and scratch-resistance, poor resistance to chemicals and soiling, as well as with edge zones of poor definition. Furthermore, these laser marking processes are limited to very few shades.

A laser marking process has now been found which makes it possible to produce a freely programmable marking on plastics objects of any kind in almost any suitable shades.

Accordingly, the present invention relates to a process for the coloured laser marking of plastics objects of any desired shape, which process comprises
a) coating the object to be marked with a soluble lacquer film containing at least one colouring component,
b) irradiating the coated object, after drying said film, with a continuously excited laser such that the laser beam is directed to the surface of the object to be marked in accordance

with the form of the marking which it is desired to effect, and such that the film and the surface of the object directly adjacent soften at the irradiated areas and the colouring component penetrates the surface of the plastics object, and

c) dissolving the residual non-irradiated film with a solvent such that a visual coloured contrast marking remains at the irradiated areas of the plastics object.

The plastics object may be of natural or synthetic origin. Such material may comprise, for example, rubber or modified natural materials, for example chlorinated rubber, or cellulose derivatives such as cellulose esters or cellulose ethers and, in particular, man-made organic polyplastics, that is to say, plastics which are obtained by polymerisation, polycondensation and polyaddition. The following products may be mentioned in particular as belonging to this class of plastics: polyolefins such as polyethylene, polypropylene, polybutylene or polyisobutylene, polystyrene, polyvinyl chloride, and polyvinylidene chloride, the fluorinated polymers such as polytetra-fluoroethylene, and polyvinyl acetals, polyacrylonitrile, polyacrylates, polymethacrylates or polybutadiene, and copolymers thereof, in particular ABS or EVA; polyesters, in particular high molecular esters of aromatic polycarboxylic acids and polyfunctional alcohols: polyamides, polyimides, polycarbonates, polyurethanes, polyethers such as polyphenylene oxide, and also polyacetals; the condensates of formaldehyde and phenols (phenolic plastics), and the condensates of formaldehyde and urea, thiourea and melamine (aminoplasts); the polyadducts and polycondensates of epichlorohydrin and diols or polyphenols known as epoxy resins; and also the unsaturated polyesters used as surface-coating resins, for example maleic resins. It must be emphasised that not only the homogeneous compounds can be used in the practice of this invention, but also mixtures of polyplastics, as well as co-condensates and copolymers, for example those based on butadiene.

Plastics materials which are particularly suitable for the process of this invention are polyolefins, polyvinyl esters such as polyvinyl acetals, and also polyacrylates and polymethacrylates, polyesters, polyamides, polyimides, polycarbonates, polyurethanes, polyethers, preferably polyphenylene oxides, as well as polyacetals, phenolic plastics, aminoplasts or epoxy resins.

The most suitable plastics materials are polyacrylates, polymethacrylates, polyesters and polycarbonates.

The plastics object may be uncoloured or, if desired, coloured, in which latter case the suitable colourants known to the skilled person may be used. In principle, all colouring components listed hereinbelow may be used as colourants.

Suitable colouring components for the process of this invention are inorganic and organic pigments as well as polymer-soluble dyes, especially those that absorb in the visible range.

Examples of inorganic pigments are white pigments such as titanium dioxides (anatas, rutile), zinc oxide, antimony trioxide, zinc sulfide, lithopones, basic lead carbonate, basic lead sulfate or basic lead silicate, and also other coloured metal oxides such as iron oxides, nickel antimony titanate, chromium antimony titanate, manganese blue, manganese violet, cobalt blue, cobalt chromium blue, cobalt nickel grey or ultramarine blue, Berlin blue, lead chromates, lead sulfochromates, bismuth vanadates, molybdate orange and molybdate red, as well as metal sulfides such as cadmium sulfide, arsenic disulfide, antimony trisulfide or cadmium sulfoselenides, zirconium silicates such as zirconium vanadium blue and zirconium preseodyme yellow, and also carbon black or graphite.

Examples of organic pigments are azo, azomethine, methine, anthraquinone, indanthrone, pyranthrone, flavanthrone, benzanthrone, phthalocyanine, perinone, perylene, dioxazine, thioindigo, isoindoline, isoindolinone, quinacridone, pyrrolopyrrole or quinophthalone pigments, and also metal complexes, for example of azo, azomethine or methine dyes or metal salts of azo compounds.

Suitable polymer-soluble dyes are, for example, disperse dyes such as those of the anthraquinone series, for example hydroxyanthraquinones, aminoanthraquinones, alkylaminoanthraquinones, cyclohexylaminoanthraquinones, arylaminoanthraquinones, hydroxyaminoanthraquinones or phenylmercaptoanthraquinones, as well as metal complexes of azo dyes, in particular 1:2 chromium or cobalt complexes of monoazo dyes, and fluorescent dyes such as those of the coumarin, naphthalimide, pyrazoline, acridine, xanthene, thioxanthene, oxazine, thiazine or benzthiazole series.

The polymer-soluble dyes are preferably used in combination with fillers and/or pigments, in particular with inorganic pigments such as titanium dioxide.

In the practice of this invention, the inorganic or organic pigments or polymer-soluble dyes can be used singly or as mixtures, conveniently with or without pigment additives.

Care must only be taken that they are compatible with the plastic film employed.

Suitable pigment additives are typically fatty acids of at least 12 carbon atoms, for example stearic acid or behenic acid and the amides, salts or esters thereof such as magnesium stearate, zinc stearate, aluminium stearate or magnesium behenate, and also quaternary ammonium compounds such as tri(C_1-C_4)alkylbenzylammonium salts, waxes such as polyethylene wax, resin acids such as abietic acid, colophonium soap, hydrogenated or dimerised colophonium, C_{12}-C_{18}-paraffin disulfonic acids or alkylphenols.

Preferred colouring components of this invention are inorganic coloured pigments and metal complexes of azo, azomethine or methine dyes, as well as azo, azomethine, methine, anthraquinone, phthalocyanine, perylene, dioxazine, thioindigo, isoindoline, isoindolinone, quinacridone or pyrrolopyrrole pigments.

Most preferred in the practice of this invention are heat-resistant colouring components.

Typical examples of colouring components suitable for use in the process of this invention are copper phthalocyanines, mono- and disazo pigments of the acetoacetarylide, β-oxynaphtharylide and 3-methyl-1-phenylpyrazol-5-one series, and also metal salts of sulfonated α-phenylazo-β-oxy-3-naphthoic acids, nickel, cobalt or copper complex pigments, as well as heat-resistant polymer-soluble dyes of the anthraquinone series.

The lacquer film of this invention conveniently contains the colouring component in an amount of 0.01 to 15% by weight, preferably of 1 to 8% by weight, based on the dry film.

If the plastics object is coloured, then a coloured marking is formed consisting of a combination of the colour of the colouring component of the invention and of the colourant present in the plastics object.

The lacquer film may also be of natural or synthetic origin, in which case it can be prepared from materials in dissolved form as film former or binder. It may be selected from modified natural materials such as cellulose derivatives, for example cellulose esters or cellulose ethers such as nitrocellulose, acetyl cellulose, cellulose propionate, cellulose acetobutyrate, ethyl cellulose, or mixtures of such substances; and also polyvinyl acetate, polyvinyl propionate, polyvinyl alcohol, polyvinyl acetals such as polyvinyl butyral,

polyacrylates and polymethacrylates, preferably polymethylmethacrylate, polymethylacrylate, polyethylmethacrylate, polybutyl acrylate and polyisobutyl acrylate, as well as mixtures thereof; also polyvinyl pyrrolidone, polyamides, polyvinyl copolymers such as polyvinyl chloride/polyvinyl acetate, spirit-soluble resins such as shellacs; as well as urea/formaldehyde resins, air-drying oils, for example linseed oils, phenolic resins, resin-modified phenolic resins, maleic acid resins, alkyd resins, ketone resins, polyurethanes, epoxy resins, polyesters and starch derivatives such as dextrin.

The lacquer film can also be prepared from materials in monomeric form, for example monomeric radically curing acrylates.

Preferred film-forming materials for the process of this invention are nitrocellulose, ethyl cellulose, cellulose propionate, cellulose acetobutyrate, polyvinyl butyral, polyacrylates and polymethacrylates, vinyl chloride/vinyl acetate copolymers, polyvinyl alcohol, polyesters, polyurethane or an epoxy resin.

The preparation of the plastics objects is effected by methods which are known per se, for example by incorporating the required components, for example the organic material and the usual additives, which may be in the form of a masterbatch, into the substrates using extruders, roll mills, mixing or grinding machines. The resultant material is then brought into the desired final form by methods which are known per se, for example calendering, moulding, extruding, coating, casting or by injection moulding. It is often desirable to incorporate plasticisers into the organic material before processing in order to produce non-brittle mouldings or to diminish their brittleness. Suitable plasticisers are, for example, esters of phosphoric acid, phthalic acid or sebacic acid. The plasticisers may be incorporated before or after working colouring components into the polymers.

Depending on the end use, further modifiers may be added to the organic plastics material, for example fillers such as kaolin, mica, feldspar, wollastonite, aluminium silicate, barium sulfate, calcium sulfate, chalk, calcite and dolomite, as well as light stabilisers, antioxidants, flame retardants, heat stabilisers, glass fibres or processing auxiliaries conventionally employed in the processing of plastics and known to the skilled person.

The lacquer film is applied to the plastics object by methods which are known per se, for example by applying a printing ink by the relief printing, intaglio printing, flat printing or screen printing method. Thus, for example, the film-forming material and the colouring

component and optionally together with further film additives are finely dispersed or dissolved in a joint organic solvent or mixture of solvents. The procedure may be such that the individual components, or also several components jointly, are dispersed or dissolved and then all the components are combined. The homogenised coloured film material is then applied to the object to be marked by one of the printing methods referred to above and dried, and the resultant film, conveniently having a thickness from 5 to 50 µm, is then marked by the process of the invention.

The film may also be applied to the plastics object, for example, by doctor coating, whirl-coating, immersion, spraying or brushing.

It can be advantageous to coat only a portion of the object with the film, expediently only that portion of the surface necessary for the type and size of the marking.

Energy-rich sources such as continuous lasers are used for marking. The procedure comprises applying the energy source to the surface of the material to be marked, according to the form of the graphic symbols to be applied and, as necessary, focussing said energy source such that a contrast marking is induced at the irradiated areas. Preferably the marking device will direct the laser beam vertically to the surface of the object to be marked.

Examples of laser sources are continuously excited or continuous wave lasers, for example on the basis of CW Nd:YAG lasers with frequency multiplier, or CW ion lasers (Ar, Kr), or high-capacity pulsed semiconductor lasers which emit visible light direct or by frequency doubling, and also gas lasers such as CO_2 lasers.

It is advantageous to use intensities of 0.1 kilowatt per cm^2 to 1 megawatt per cm^2.

It is preferred to use a continuous CO_2 laser, or an argon ion laser in the visible range of the spectrum.

The following table lists a number of commercially available lasers which may be suitable in the practice of this invention.

Table:

Type/Representative	Examples of commercially available types	Principal wavelength (subsidiary wavelengths) [nm]
Semiconductor diode laser	Spectra Physics SDL 2450	ca. 800
" Array (with frequency doubler)	STANTEL Typ LF 100	ca. 905 (402)
gas laser CO_2	SYNRAD Mod. 48 Andromeda SL-20	ca. 9000-11000
ion laser argon laser	Spectra Physics Mod. 2020 or Mod. 2016	514; 488 (477, 497)
solid-state laser (with frequency doubler)	Spectra Physics Mod. 3000	1064 (532)

In the process of this invention, marking is effected with, for example, a continuous CO_2 laser at an intensity of ca. 4 watt.

Lasers whose parameters can be readily adjusted, for example pulse content and pulse duration, permit the best possible adaptation to the requirements of the materials to be marked.

The best wavelength to be selected for radiation is that at which the film and the plastics

object to be marked, or the colouring component, absorb more than half of the laser radiation in a layer thickness of ca. 50 microns. Softening will be understood as meaning the state in which the plastics material becomes soft as well as the state in which the material is fused.

Three different methods are suitable for laser marking in the practice of this invention: the mask method, the linear marking method and the dot matrix method. In these last two mentioned methods (dynamic focussing), the laser is preferably combined with a laser deflection system, so that the object can be marked with any, e.g. computer-programmed, digits, letters and special symbols.

The choice of laser system in respect of capacity depends basically on the marking method employed. High capacity is preferred for mask exposure. Average to low capacities are preferred for producing markings that require dynamic focusing. Beam deflection can be effected e.g. acousto-optically, holographically, with galvo-mirrors or polygon scanners. Dynamic focusing makes possible an extremely flexible marking, as the marks can be produced electronically.

Dissolving the film at the unmarked areas is effected by methods which are known per se, for example by using a solvent or solvent mixture in which the lacquer film is readily soluble and the plastics object is not. Aqueous-alkaline solutions or aqueous-alcoholic alkaline solutions may also be used, for example for polyacrylate films which contain carboxyl groups. Illustrative of suitable solvents are: methanol, ethanol, n-propanol, isopropanol, butanol, petroleum ether, aromatic hydrocarbons such as toluene, and also ketones such as cyclohexanone, acetone, methyl ethyl ketone and methyl isobutyl ketone, ethyl acetate, butyl acetate, tetrahydrofuran, glycol esters and glycol ethers, as well as aliphatic hydrocarbons, for example n-heptane, n-octane, n-decane and n-dodecane, and mixtures of such solvents.

A very wide range of markings can be produced by the process of this invention. Examples are: variable text programming of numerical symbols by inputting text with a video display unit, text programs of standard symbols or special symbols such as monograms, as well as initials and inscriptions, identification marks, logos, or frequently recurring data, continuous piece numbering, input of measurable variables, input of a stored program, linear marking or also decorations.

It is also possible in the process of this invention to mark a very wide range of plastics objects such as mouldings, boards, sheets and films. Illustrative of such objects are ribbons, plates, tubes and profiles, keys and plastics-coated electronic components.

Typical utilities are the marking of circuits, printed circuit boards, printed circuits, active and passive electronic components, encapsulated high voltage transformers, plug sockets, casings, mechanical components of precision technology and of the watch-making industry, automotive components, keyboards, control knobs, electronic components, cables, tubes, sheets and films, as well as credit cards and identity cards.

The process of this invention makes it possible to produce any combination of colour contrast markings which are indelible and therefore abrasion- and scratch proof. The markings obtained in this invention are also corrosion-proof, dimensionally stable, free from deformation, fast to light, heat and weathering, easily legible, and have good edge definition. In addition, there is virtually no impairment of the mechanical and physical properties of the marked object, for example mechanical strength and chemical resistance. The impression depth of the marking depends on the marked material and is usually less than 1 mm, often less than 0.2 mm. Hence it is possible to produce markings which are detectable by the eye and which do not impair the mechanical properties of a workpiece of sufficient thickness.

In the following Examples parts are by weight, unless otherwise indicated.

<u>Examples 1-3</u> (Marking a polyester)
A) A coloured layer is prepared by dissolving an acrylate lacquer in ®Dowanol PM (2-methoxyethanol; corresponds to a 46 % acrylate solution), which acrylate lacquer consists of a mixture of

40 g of cyclohexylmethacrylate,
80 g of butyl acrylate,
40 g of methacrylic acid, and 40 g of acrylic acid, and which mixture is polymerised in a mixture of 30 ml of methyl cellosolve and 300 ml of methyl ethyl ketone for 30 hours at 80°C.

30 g of this solution are thoroughly mixed with 1.5 g of each of the pigments listed below for 3 hours at 50°C with a magnetic stirrer. Each coloured air-drying lacquer is applied

with an applicator for 12 µm wet film thickness to a 2 mm thick thermoplastic plate (®Crastin S600; polyester; Ciba-Geigy AG) and dried for 1 hour at 50°C.

Pigments used:
®Cromophtal Scarlet RN (C.I. Pigment Red 166; Ciba-Geigy AG);
®Cromophtal Green GFN (C.I. Pigment Green 7; Ciba-Geigy AG);
®Microlith Blue 4G-WA (pigment preparation containing C.I. Pigment Blue 15:3 and a polyacrylic resin; Ciba-Geigy AG).

B) Marking is made by focussing the beam of an argon laser (514 nm, 0.5 W output) with a vector marking device (®Gretag 6210) [lens aperture 200 mm] and guiding it by computer control over the coated surface of the thermoplastic plate at a speed of 25 mm/s.

C) After it has been marked, the plate is developed (i.e. the non-irradiated film is treated) in an aqueous alkaline solution (1% Na_2CO_3 and 1% ethanol) until the coloured film has been completely removed from the unmarked areas.

A distinct, decorative marking in the original hue of the pigment (scarlet, green or blue) forms on the white background of the substrate. The marking is resistant to moderate mechanical stress and mild solvents (alcohol).

Examples 4-6: In accordance with the procedure described in Examples 1-3, transparent polycarbonate plates are coated instead of ®Crastin plates. Marking and developing are carried out as in Examples 1-3. The resultant corresponding coloured markings on the transparent material can be observed either on a bright background or in transmitted light.

Examples 7-9: Plates are prepared in accordance with Examples 1-3, except that a continuous wave CO_2 laser (wavelength 10.6 µm) [intensity 3-4 W; marking speed 100 mm/sec]. Markings are also obtained in the hue of the pigment used on a white background.

Examples I to XIII: The following plastics materials are processed to plates measuring 3 x 8 cm (length x width) and having a thickness of 2 mm by the method with which the skilled person is familiar:

<u>Examples No:</u>

I polypropylene ®Simona PP-Devu (Simona GmbH, FRG);

II polycarbonate ®Lexan (General Electric Plastics);

III ABS clear, ®Terluran 877M (BASF);

IV ABS white (with TiO_2), ®Terluran 877M (BASF);

V PMMA ®Plexiglas (Bayer);

VI PMMA white, ®Plexiglas (Bayer);

VII PVC grey, ®Trovidur EN (Dynamit Nobel);

VIII PVC white, ®Trovidur ET (Dynamit Nobel);

IX PVC transparent, ®Trovidur ET (Dynamit Nobel);

X PBTP natural, ®Crastin S600 (Ciba-Geigy AG);

XI PBTP orange, ®Crastin S600 (Ciba-Geigy AG) with 0.3 % ®Cadmopur Orange;

XII PBTP yellow, ®Crastin S600 (Ciba-Geigy AG) with 0.3 % ®Cadmopur Gelb;

XIII polyamide ®Rilsan Besno P40.

The following coloured lacquers are prepared for coating these sample plates:

1. A solution of 2 g of polyvinyl butyral ®Mowital B 60 T (Hoechst) in 18 ml of ethanol is mixed thoroughly with 4% (based on the weight of the polymer) of one of the following pigments:
a) ®Microlith Blue 4G-WA (C.I. 74 160);
b) ®Irgalith Blue GLSM (C.I. 74 160);
c) ®Microlith Red 2B-WA (C.I. Pigment Red 221).

2. A solution of 3 g of polymethylmethacrylate ®Elvacite 2043 (DuPont) in 20 ml of ethanol is mixed with 4% of one of the following dyes until the dye has completely dissolved:
a) ®Filester Red 2973-A (anthraquinone derivative, Ciba-Geigy AG);
b) ®Oracet Yellow GHS (C.I. 58 840);
c) ®Orosol Red 3GL (C.I. Solvent Red 130).

3. A solution of ca. 1.25 g of polycarbonate ®Luvican M 170 (BASF) in a 1:1 mixture of chloroform/toluene is thoroughly mixed with 8% (based on dry polymer) of coloured pigment ®Microlith Blue 4G-WA (C.I. 74 160).

For better adhesion to the above substrates, 0.5% of additive/wetting agent No. 29,

available from Dow-Corning, can be added to the lacquers of Examples 1 and 2 a)-c).

The above lacquers are then applied with an applicator for 100 µm wet film thickness to the rectangular flat plates made from the plastics materials I to XIII listed above.

The coated plates are marked in accordance with Example 1 with letters 2-4 mm high, and next to them rectangles measuring 4 x 20 mm (length x width) are drawn using an argon laser and a CO_2 laser.

The marking with the argon laser is effected in accordance with Example 1B, and that with the CO_2 laser in accordance with Examples 7-9.

The tests and results are summarised in the following table, the figures listed in the last column of which represent a visual rating and are to be interpreted as follows.

The rating takes into account the following factors: colour contrast, relief formation and shade of the marking. The figures denote:

4 : very good with respect to all three factors
3 : very good with respect to at least two factors
2 : good with respect to at least two factors
1 : good with respect to at least one factor.

Table

Example	Plastic/ Substrate	Coating Lacquer number	Marking Laser, intensity or marking speed	Marking Rating
I	PP	1a	argon 500 mW	2
I	PP	1c	argon 200 mW	1
I	PP	1c	CO_2 100 mm/sec	2
I	PP	2b	argon 800 mW	3
I	PP	2a	argon 400 mW	3
I	PP	2a	CO_2 150 mm/sec	2
II	PC	1c	CO_2 100 mm/sec	2
II	PC	1c	argon 200 mW	2
II	PC	2c	argon 100 mW	1
III	ABS, clear	1a	argon 1000 mW	2
III	ABS, clear	1c	argon 200 mW	1
IV	ABS, white	1a	argon 500 mW	2
IV	ABS, white	1c	argon 200 mW	2
V	PMMA, transp.	1a	argon 800 mW	3
V	PMMA, transp.	1a	CO_2 100 mm/sec	2
V	PMMA, transp.	1c	argon 200 mW	1
VI	PMMA, white	1a	argon 1500 mW	2
VI	PMMA, white	1a	CO_2 100 mm/sec	2
VI	PMMA, white	2c	argon 100 mW	2
VI	PMMA, white	2c	CO_2 150 mm/sec	2
VII	PVC, grey	1a	argon 200 mW	1
VII	PVC, grey .	1a	CO_2 100 mm/sec	1
VII	PVC, grey	2a	argon 100 mW	3
VII	PVC, grey	2b	argon 200 mW	2
VII	PVC, grey	2c	argon 200 mW	2
VII	PVC, grey	2a	CO_2 200 mm/sec	3
VI	PVC, grey	2b	CO_2 200 mm/sec	2
VII	PVC, grey	2c	CO_2 200 mm/sec	2
VIII	PVC, white	1c	argon 25 and 50 mW	3

Table (Continuation)

Example	Plastic/ Substrate	Coating Lacquer number	Marking Laser, intensity or marking speed	Marking Rating
IX	PVC, transp.	1c	argon 50 mW	2
X	PBTP, natural	1a	argon 1,5 W	4
X	PBTP, natural	1b	argon 200 mW	3
X	PBTP, natural	1c	argon 500 mW	4
X	PBTP, natural	1a	CO_2 100 mm/sec	2
X	PBTP, natural	1b	CO_2 100 mm/sec	2
X	PBTP, natural	1c	CO_2 150 mm/sec	2
X	PBTP, natural	2a	CO_2 100 mm/sec	4
X	PBTP, natural	3a	argon 200 mW	2
XI	PBTP, orange	1a	argon 1000 mW	2
XI	PBTP, orange	3a	argon 100 mW	2
XII	PBTP, yellow	1c	argon 1000 mW	1
XIII	PA	2a	argon 600 mW	2
XIII	PA	1c	CO_2 125 mm/sec	2

Note:
Intensity of the CO_2 laser: 3-4 watt in all experiments.

What is claimed is:

1. A process for the coloured laser marking of plastics objects of any desired shape, which process comprises
a) coating the object to be marked with a soluble lacquer film containing at least one colouring component,
b) irradiating the coated object, after drying said film, with a continuously excited laser such that the laser beam is directed to the surface of the object to be marked in accordance with the form of the marking which it is desired to effect, and such that the film and the surface of the object directly adjacent soften at the irradiated areas and the colouring component penetrates the surface of the plastics object, and
c) dissolving the residual non-irradiated film with a solvent such that a visual coloured contrast marking remains at the irradiated areas of the plastics object.

2. A process according to claim 1, which comprises using as a continuous laser a CO_2 laser, or an argon laser in the visible range of the spectrum.

3. A process according to claim 1, wherein the material of the plastics object is selected from the group consisting of polyolefins, polyvinyl esters, polyacrylates and polymethacrylates, polyesters, polyamides, polyimides, polycarbonates, polyurethanes, polyethers, polyacetals, phenolic plastics, aminoplasts or epoxy resins.

4. A process according to claim 1, wherein the colouring component absorbs in the visible range.

5. A process according to claim 1, wherein the colouring component is an inorganic or organic pigment or a polymer-soluble dye.

6. A process according to claim 5, wherein the inorganic pigment is a white pigment, a coloured metal oxide, Berlin blue, a lead chromate, lead sulfochromate, bismuth vanadate, molybdate orange, molybdate red, a metal sulfide or a zirconium silicate, carbon black or graphite.

7. A process according to claim 5, wherein the organic pigment is an azo, azomethine, methine, anthraquinone, indanthrone, pyranthrone, flavanthrone, benzanthrone,

phthalocyanine, perinone, perylene, dioxazine, thioindigo, isoindoline, isoindolinone, quinacridone, pyrrolopyrrole or quinophthalone pigment, or also a metal complex or a metal salt of an azo compound.

8. A process according to claim 5, wherein the colouring component is an inorganic coloured pigment or a metal complex of an azo, azomethine or methine dye, or an azomethine, methine, anthraquinone, phthalocyanine, perylene, dioxazine, thioindigo, isoindoline, isoindolinone, quinacridone or pyrrolopyrrole pigment.

9. A process according to claim 1, wherein the polymer-soluble dye is a disperse dye of the anthraquinone series, a metal complex of an azo dye, or a fluorescent dye of the coumarin, naphthalimide, pyrazoline, acridine, xanthene, thioxanthene, oxazine, thiazine or benzene series.

10. A process according to claim 1, wherein the colouring component is used in an amount of 0.01 to 15% by weight, based on the dry film.

11. A process according to claim 1, wherein the lacquer film is prepared from a cellulose derivative, a polyvinyl acetate, a polyvinyl propionate, a polyvinyl alcohol, a polyvinyl acetal, a polyacrylate or polymethacrylate, a polyvinyl pyrrolidone, a polyamide, a polyvinyl copolymer, a spirit-soluble resin, a urea/formaldehyde resin, an air-drying oil, a phenolic resin, a resin-modified phenolic resin, a maleic acid resin, an alkyd resin, a ketone resin, a polyurethane, an epoxy resin, a polyester or a starch derivative.

12. A process according to claim 11, wherein the film is prepared from nitrocellulose, ethyl cellulose, cellulose propionate, cellulose acetobutyrate, polyvinyl butyral, a polyacrylate or polymethacrylate, a vinyl chloride/vinyl acetate copolymer, a polyvinyl alcohol, a polyester, a polyurethane or an epoxy resin.

13. A process according to claim 1, wherein the residual non-irradiated film is removed by dissolving it with an aqueous-alkaline or aqueous-alcoholic alkaline solution.

14. Material marked by a process as claimed in any of the preceding claims.

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